

1351528

PATENT SPECIFICATION

(11)

351528



- (21) Application No. 18550/71 (22) Filed 2 June 1971
(31) Convention Application No. P 20 27 465.1
(32) Filed 4 June 1970 in
(33) Germany (DT)
(44) Complete Specification published 1 May 1974
(51) International Classification C07C 143/72 C07D 27/18
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C2C 1342 200 20Y 215 220 227 22Y 247 250 251 25Y
30Y 313 31Y 339 342 34Y 351 352 366 368
385 510 511 512 513 514 51Y 520 522 52X
52Y 699 SB SC

SPECIFICATION NO 1351528

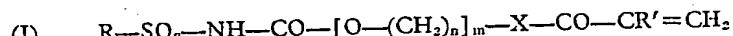
By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of HOECHST AKTIENGESELLSCHAFT, A Body Corporate organised according to the Laws of Germany, of 6230 Frankfurt/Main 80, Germany.

R 78386/1

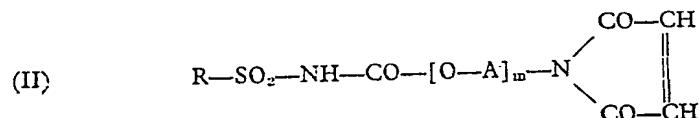
THE PATENT OFFICE

10 isocyanates with polymers containing hydroxyl groups or amino groups (see U.S. Patent Specification No. 3,422,075). 10

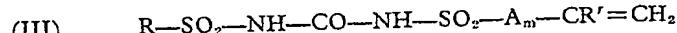
The present invention provides N-carbonyl sulphonamides substituted by unsaturated groups, which correspond to one of the following formulae:



15 or



or



20 wherein 20
R is an alkyl or alkoxy radical with 1 to 6, preferably 1 to 3, carbon atoms, which may be substituted by 1 to 3 halogen atoms, preferably chlorine atoms, or by a cycloalkyl radical or an aryl radical or aryloxy radical each with 6 or 10 carbon atoms in the nucleus, which may be substituted up to three times by halogen atoms, preferably chlorine atoms, and/or by alkyl or alkoxy radicals each with 1 to 6 carbon atoms, preferably with 1 to 3 carbon atoms,
25 R' is a hydrogen atom or a methyl radical,
X is an oxygen atom or an imino group,
A is a phenylene radical or an alkylene radical with 1 to 4, preferably 1 or 2 carbon atoms,
30 n is an integer from 1 to 4, preferably 1 or 2, and
m is 1, or may be 0 when X stands for an amino group in formula I or may be 0 in formula II.

SPECIFICATION AMENDED - SEE ATTACHED SLIP

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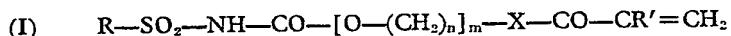
(54) N-CARBONYL SULPHONAMIDES SUBSTITUTED BY
 UNSATURATED GROUPS, AND A PROCESS FOR THEIR
 MANUFACTURE

(71) We, KALLE AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 190—196 Rheingaustrasse, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

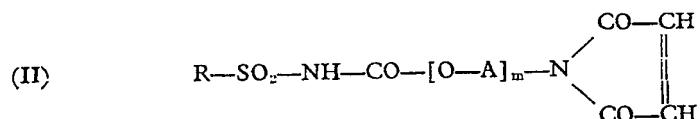
This invention is concerned with N-carbonyl sulphonamides substituted by unsaturated groups, and a process for their manufacture.

The reaction of sulphonyl isocyanates with H-acidic compounds has been known for a long time (see Ber. 37, 1904, page 690). Further, it is known to react sulphonyl isocyanates with polymers containing hydroxyl groups or amino groups (see U.S. Patent Specification No. 3,422,075).

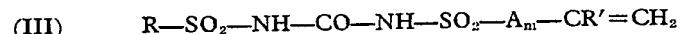
The present invention provides N-carbonyl sulphonamides substituted by unsaturated groups, which correspond to one of the following formulae:



15 or



or



wherein

20 R is an alkyl or alkoxy radical with 1 to 6, preferably 1 to 3, carbon atoms, which may be substituted by 1 to 3 halogen atoms, preferably chlorine atoms, or a cycloalkyl radical or an aryl radical or aryloxy radical each with 6 or 10 carbon atoms in the nucleus, which may be substituted up to three times by halogen atoms, preferably chlorine atoms, and/or by alkyl or alkoxy radicals each with 1 to 6 carbon atoms, preferably with 1 to 3 carbon atoms,

25 R' is a hydrogen atom or a methyl radical,

X is an oxygen atom or an imino group,

A is a phenylene radical or an alkylene radical with 1 to 4, preferably 1 or 2 carbon atoms,

30 n is an integer from 1 to 4, preferably 1 or 2, and

m is 1, or may be 0 when X stands for an amino group in formula I or may be 0 in formula II.

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The present invention further provides a process for the manufacture of substituted N-carbonyl sulphonamides, wherein a sulphonyl isocyanate of the formula



wherein

5 R has the meaning given above

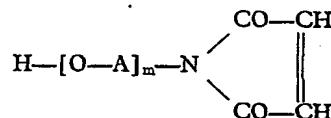
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is reacted, in an inert gas atmosphere and at temperatures between 0 and 100°C, with an H-acidic unsaturated compound of one of the following formulae:



or

10



10

or



wherein

R', X, A, n and m have the meanings given above.

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Preferred sulphonyl isocyanates to be used according to the invention are: alkyl sulphonyl isocyanates, cycloalkyl sulphonyl isocyanates, alkoxy sulphonyl isocyanates, halogenalkyl sulphonyl isocyanates, halogenalkoxy sulphonyl isocyanates, arylsulphonyl isocyanates, aryloxy sulphonyl isocyanates, and aryl or aryloxy sulphonyl isocyanates substituted by halogen atoms, alkyl radicals, and/or alkoxy radicals, for example methylsulphonyl isocyanate, β -chloroethyl sulphonyl isocyanate, cyclohexyl sulphonyl isocyanate, phenyl-sulphonyl isocyanate, α -tolylsulphonyl isocyanate, m -tolylsulphonyl isocyanate, p -tolylsulphonyl isocyanate, 2-chlorophenyl sulphonyl isocyanate, 3-chlorophenyl sulphonyl isocyanate, 4-chlorophenyl sulphonyl isocyanate, 4-bromophenyl sulphonyl isocyanate, 4-fluorophenyl sulphonyl isocyanate, 3,4-dimethyl-phenyl sulphonyl isocyanate, 3,5-dimethylphenyl sulphonyl isocyanate, 2,4,6-trimethyl phenyl sulphonyl isocyanate, 4-ethylphenyl sulphonyl isocyanate, 3,4-dichlorophenyl sulphonyl isocyanate, 2,5-dichlorophenyl sulphonyl isocyanate, 3,5-dichlorophenyl sulphonyl isocyanate, 4-methoxyphenyl sulphonyl isocyanate, naphthalene-1-sulphonyl isocyanate, phenoxy sulphonyl isocyanate, 2-methylphenoxy-sulphonyl isocyanate, 3-methylphenoxy sulphonyl isocyanate, 4-methylphenoxy sulphonyl isocyanate, 2,3-dimethyl phenoxy sulphonyl isocyanate, 2,4-dimethyl phenoxy sulphonyl isocyanate, 2,6-dimethyl phenoxy sulphonyl isocyanate, 4-chloro phenoxy sulphonyl isocyanate, 4-methoxyphenoxy-sulphonyl isocyanate, 4-tert-butyl phenoxy sulphonyl isocyanate, 4-cyclohexyl phenoxy sulphonyl isocyanate and 2,4,6-trimethylphenoxy sulphonyl isocyanate.

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The following compounds may be used as H-acidic unsaturated compounds: (meth)acrylic acid, (meth)acrylic acid- ω -hydroxy alkyl ester, (meth)acrylic amide, (meth)acrylic acid-N-(ω -hydroxylalkyl)-amide, maleic imide, N-(ω -hydroxylalkyl)-amide, maleic imide, N-(ω -hydroxylalkyl)-maleic imide, N-hydroxyphenyl-maleic imide, ω -alkene-sulphonamide, vinylphenyl-sulphonic acids and vinylphenyl sulphonic amides, e.g. acrylic acid- β -hydroxyethyl ester, acrylic acid- γ -hydroxypropyl ester, methacrylic acid- β -hydroxy ethyl ester, methacrylic ester- γ -hydroxypropyl ester, methacrylic acid- δ -hydroxybutyl ester, N-methylol-acrylamide, N-(β -hydroxyethyl)-acrylamide, N-methylol-methacrylamide, N-methylol-maleicimide, N-(p -hydroxyphenyl)-maleicimid, and styrene- p -sulphonamide.

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The process of the invention is performed at normal pressure and temperatures between 0 and 100°C, preferably between 20 and 80°C, most advantageously at room temperature. The process must be carried out under anhydrous conditions, i.e. with the exclusion of moisture.

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Advantageously, the process of the invention is performed by dissolving one of the reaction components in an anhydrous aromatic hydrocarbon, preferably benzene

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or toluene, or in an anhydrous ether, preferably diethyl ether of 1,4-dioxan, and then cautiously adding, drop by drop and at room temperature, a solution of the second reaction component in the same or another solvent, while agitating and passing an inert gas, preferably nitrogen, over the reaction mixture. The reaction product is isolated either by evaporation of the solvent, or by cooling to 0°C, or by adding a precipitating agent to the reaction mixture, for example an aliphatic hydrocarbon, such as *n*-hexane or *n*-heptane. The reaction products may be recrystallized from a suitable solvent, e.g. methanol, ethanol, toluene, or diisopropyl ether.

The compounds according to the invention may be designated either as N-sulphonyl carbamic acid esters (N-sulphonyl urethanes), or as N-sulphonyl ureas. The following are examples of such compounds: N-(*p*-tolylsulphonyl)-carbamic acid-(β -methacryloyloxy)-ethyl ester, N-(*p*-tolylsulphonyl)-carbamic acid-(γ -methacryloyloxy)-propyl ester, N-(β -chloroethyl sulphonyl)-carbamic acid-(β -methacryloyloxy)-ethyl ester, N-(*p*-tolyloxy-sulphonyl)-carbamic acid-(β -methacryloyloxy)-ethylester, N-(2,6 - dimethylphenoxy-sulphonyl)-carbamic acid - (β - methacryloyloxy) - ethyl ester, N-(*p*-tolylsulphonyl)-carbamic acid-(acrylamido)-methyl-ester, N-(*p*-tolylsulphonyl)-carbamic acid-(maleimido)-methyl ester, N-(β -chloroethyl sulphonyl)-carbamic acid-(maleimido)-methyl ester, N-(*p*-tolylsulphonyl)-N'-acryloyl-urea, N-(*p*-tolyloxysulphonyl)-N'-acryloyl-urea, N-(*p*-tolylsulphonyl)-N'-(*p*-vinylphenylsulphonyl)-urea, N-(*p*-tolylsulphonyl)-N'-maleoyl-urea, N-(β -chloroethylsulphonyl)-N'-maleoyl-urea, and N-(*p*-tolylsulphonyl)-carbamic acid-(*p*-N'-maleimido)-phenyl ester.

The compounds according to the invention are capable of radical polymerization and are used for the production of homopolymers or copolymers useful as flocculation agents, as dispersing agent, or as binders for light-sensitive layers.

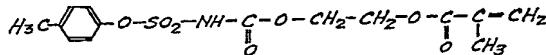
The following Examples illustrate the invention; parts and percentages are by weight:

Example 1

65 parts of β -hydroxy-ethyl-methacrylate are dissolved in 140 parts of anhydrous diethyl ether. Then a solution of 115 parts of *p*-methyl-phenoxy sulphonyl isocyanate in 350 parts of anhydrous diethyl ether is added dropwise, over a period of 20 minutes and at room temperature, while stirring and passing nitrogen over the reaction mixture. The mixture is cooled to 0°C and then stirred for 1 hour at this temperature. A white precipitate forms which is drawn off by suction, recrystallized from isopropyl ether, and dried in a vacuum desiccator.

Yield: 97.5%
Melting Point: 57°C

The elementary analysis of the N-(*p*-methylphenoxy-sulphonyl)-carbamic acid-(β -methacryloyloxy)-ethylester thus obtained, of the formula



yields the following percentages, for an empirical formula of C₁₄H₁₁NO₃S (molecular weight 343):

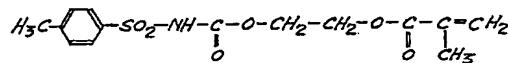
Calculated:	N 4.1	S 9.3
Found:	N 3.9	S 9.3

Example 2

A solution of 38.5 parts of β -hydroxy-ethyl-methacrylate in 45 parts of anhydrous toluene is added dropwise, over a period of 30 minutes and at room temperature, to a solution of 66 parts of *p*-tolylsulphonyl isocyanate in 70 parts of anhydrous toluene, while agitating and passing nitrogen over the reaction mixture. The reaction mixture is cooled to 0°C and stirred for one hour at this temperature. The white precipitate which forms is drawn off by suction, recrystallized from toluene, and dried in a vacuum desiccator.

Yield: 92%
Melting point: 79—80°C

The elementary analysis of the N-(*p*-tolylsulphonyl)-carbamic acid-(β -methacryloyloxy)-ether ester thus obtained, of the formula



5 yields the following percentages, for an empirical formula of $\text{C}_{14}\text{H}_{17}\text{NO}_6\text{S}$ (molecular weight 327):

Calculated:	N 4.3	S 9.8
Found:	N 4.2	S 9.8

Example 3

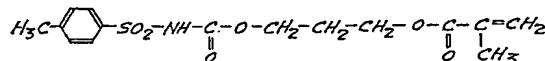
10 A solution of 42 parts of γ -hydroxy-propyl-methacrylate in 45 parts of anhydrous toluene is added dropwise, over a period of 30 minutes and at room temperature, to a solution of 66 parts of *p*-tolyl sulphonyl isocyanate in 70 parts of anhydrous toluene, while agitating and passing nitrogen over the reaction mixture. The mixture is cooled to 0°C and stirred for one hour at this temperature. The white precipitate which forms is drawn off by suction, recrystallized from toluene, and dried in a vacuum desiccator.

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Yield: 88%
Melting point: 100—103°C

The elementary analysis of the N-(*p*-tolylsulphonyl)-carbamic acid-(γ -methacryloyloxy)-propyl ester thus produced, of the formula

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yields the following percentages, for an empirical formula of $\text{C}_{15}\text{H}_{19}\text{NO}_6\text{S}$ (molecular weight 341):

Calculated:	N 4.1	S 9.3
Found:	N 3.9	S 9.4

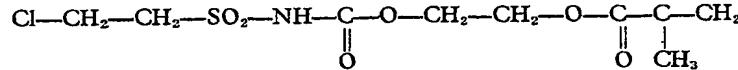
Example 4

25 11.5 parts of β -hydroxy-ethyl-methacrylate, dissolved in 22 parts of anhydrous diethyl ether, are added dropwise, over a period of 20 minutes and at room temperature, to a solution of 17 parts of β -chloroethylsulphonyl isocyanate in 22 parts of anhydrous diethyl ether, while agitating and passing nitrogen over the reaction mixture. The reaction mixture is stirred for one hour at room temperature. Then the solvent is removed by vacuum distillation, a water-white, highly viscous oil being obtained.

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Yield: 95%

35 The elementary analysis of the N-(β -chloroethylsulphonyl)-carbamic acid-(β -methacryloyloxy)-ethyl ester thus obtained, of the formula



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yields the following percentages for an empirical formula of $\text{C}_9\text{H}_{14}\text{ClNO}_6\text{S}$ (molecular weight 309.5):

Calculated:	N 4.5	S 10.3	Cl 11.5
Found:	N 4.5	S 10.3	Cl 11.8

Example 5

A solution of 39.4 parts of *p*-tolylsulphonyl isocyanate in 36 parts of anhydrous diethyl ether is added dropwise, over a period of 30 minutes and at room temperature,

to a suspension of 25.4 parts of N-methylol-maleic imide in 70 parts of anhydrous diethyl ether, while agitating and passing nitrogen over the reaction mixture. After stirring the mixture for 5 hours at room temperature, the precipitate which forms is drawn off by suction, recrystallized from toluene, and dried at 50°C in a nitrogen atmosphere.

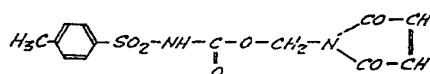
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Yield: 88%
Melting point: 160°C

The elementary analysis of the N-(*p*-tolylsulphonyl)-carbamic acid-maleimido-methyl ester thus obtained, of the formula

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yields the following percentages, for an empirical formula of C₁₃H₁₂N₂O₆S (molecular weight 324):

Calculated:	N 8.65	S 9.9
Found:	N 8.6	S 9.5

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Example 6

A solution of 34 parts of β -chloroethyl sulphonyl isocyanate in 36 parts of anhydrous diethyl ether is added dropwise, at room temperature, to a suspension of 25.4 parts of N-methylol-maleic imide in 70 parts of anhydrous diethyl ether, while thoroughly stirring and passing nitrogen over the reaction mixture. The mixture is stirred for 5 hours at room temperature, and the precipitate which forms is drawn off by suction, recrystallized from ethanol, and dried at 50°C in a nitrogen atmosphere.

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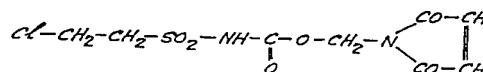
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Yield: 97%
Melting point: 140—142°C

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The elementary analysis of the N-(β -chloroethylsulphonyl)-carbamic acid maleimido methyl ester thus obtained, of the formula



yields the following percentages, for an empirical formula of C₈H₉ClN₂O₆S (molecular weight 296.5):

30

30

Calculated:	N 9.4	S 10.8
Found:	N 9.4	S 10.6

Example 7

A solution of 100 parts of *p*-tolyl sulphonyl isocyanate in 250 parts of anhydrous 1,4-dioxan is cautiously added, over a period of 20 minutes, at room temperature, to a solution of 91 parts of *p*-styryl-sulphonamide in 500 parts of anhydrous 1,4-dioxan, while agitating and passing nitrogen over the reaction mixture. The mixture is stirred for one hour at room temperature and then mixed with 650 parts of *n*-heptane. The precipitate which forms is drawn off by suction, recrystallized from toluene, and dried in a vacuum desiccator.

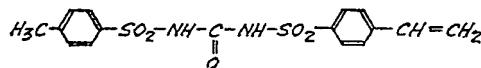
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Yield: 42%
Melting point: 125—128°C

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The elementary analysis of the N-(*p*-tolylsulphonyl)-N'-(*p*-vinyl-phenylsulphonyl)-urea thus obtained, of the formula



yields the following percentages, for an empirical formula of $C_{11}H_{16}N_2O_5S_{22}$ (molecular weight 380):

Calculated:	N 7.4	S 16.8
Found:	N 7.3	S 16.6

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Example 8

A solution of 19.6 parts of *p*-tolyl sulphonyl isocyanate in 25 parts of anhydrous 1,4-dioxan is added dropwise, over a period of 20 minutes, at room temperature, to a solution of 10 parts of N-methylol-acrylamide in 100 parts of anhydrous 1,4-dioxan, while agitating and passing nitrogen over the reaction mixture. The mixture is stirred for 1 hour at room temperature and then 330 parts of *n*-hexane are added. The precipitate which forms is drawn off by suction and dried.

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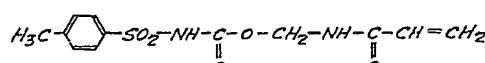
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Yield: 82.5%
Melting point: 117—119°C

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The elementary analysis of the N-(*p*-tolylsulphonyl)-carbamic acid (acrylamido)methylester thus obtained, of the formula

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yields the following percentages, for an empirical formula of $C_{12}H_{14}N_2O_5S$ (molecular weight 298):

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Calculated:	N 9.4	S 10.7
Found:	N 9.2	S 10.7

20

Example 9

While agitating and passing nitrogen over the reaction mixture, a solution of 98.5 parts of *p*-tolylsulphonyl isocyanate in 100 parts of anhydrous 1,4-dioxan is added dropwise, over a period of 30 minutes, at room temperature, to a solution of 35.5 parts of acrylamide in 250 parts of anhydrous 1,4-dioxan. The mixture is stirred for one hour at room temperature and then diluted by adding 500 parts of *n*-hexane. The precipitate which forms is drawn off by suction, recrystallized from toluene, and dried at 50°C in a nitrogen atmosphere.

25

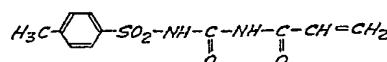
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Yield: 83%
Melting point: 155—160°C

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The elementary analysis of the N-(*p*-tolylsulphonyl)-N'-acryloyl-urea thus obtained, of the formula

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35

yields the following percentages, for an empirical formula of $C_{11}H_{12}N_2O_4S$ (molecular weight 268):

35

Calculated:	N 10.4	S 11.9
Found:	N 10.4	S 11.0

Example 10

While agitating and passing nitrogen over the reaction mixture, a solution of 19 parts of *p*-tolylsulphonyl isocyanate in 50 parts of anhydrous 1,4-dioxan is added dropwise, over a period of 20 minutes and at room temperature, to a solution of 9.7 parts of maleic imide in 100 parts of anhydrous 1,4-dioxan. The mixture is stirred for 1 hour at room temperature and then for 30 minutes at 80°C, and then the solvent is removed by vacuum distillation. The wax-like residue is spread on clay plates and dried at room temperature.

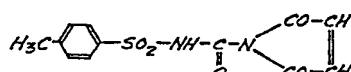
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Yield: 62%
Melting point: 120°C

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The elementary analysis of the N-(*p*-tolylsulphonyl)-N'-maleoyl-urea thus obtained, of the formula

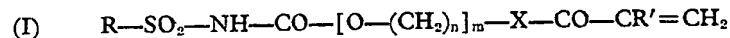


5 yields the following percentages, for an empirical formula of C₁₂H₁₀N₂O₆S (molecular weight 294):

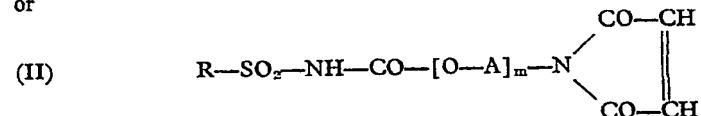
Calculated: N 9.5 S 10.9
Found: N 9.5 S 11.3

WHAT WE CLAIM IS:—

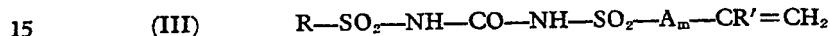
10 1. N-carbonyl sulphonamides substituted by unsaturated groups, which correspond to one of the following formulae:



or



or



wherein

20 R is an alkyl or alkoxy radical each with 1 to 6 carbon atoms, which may be substituted by 1 to 3 halogen atoms, or a cycloalkyl radical, or an aryl radical or an aryl radical or aryloxy radical each with 6 or 10 carbon atoms in the nucleus, which may be substituted up to three times by halogen atoms and/or by alkyl radicals each with 1 to 6 carbon atoms,

R' is a hydrogen atom or a methyl radical,

X is an oxygen atom or an imino group,

A is a phenylene radical or an alkylene radical with 1 to 4 carbon atoms,

25 n is an integer from 1 to 4, and

m is 1, or may be 0 when X stands for an imino group in formula I or may be 0 in formula II.

2. Any one of the compounds claimed in claim 1 and described herein.

3. A process for the manufacture of substituted N-carbonyl sulphonamides,

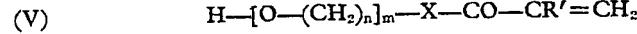
30 wherein a sulphonyl isocyanate of the formula



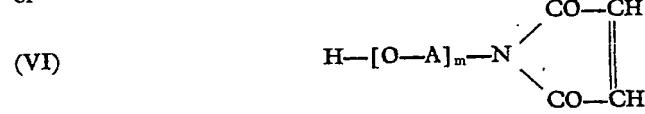
wherein

R has the meaning given in claim 1,

35 is reacted, in an inert gas atmosphere and at temperatures between 0 and 100°C, with an H-acidic unsaturated compound corresponding to one of the following formulae:



or



40 or

(VII)



wherein

 $\text{R}', \text{X}, \text{A}_m$ and m have the meanings given in claim 1.

- 5 4. A process as claimed in claim 3, substantially as described in any one of the Examples herein.
5 5. Substituted N-carbonyl sulphonamides, when made by the process claimed in claim 3 or 4.

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